



Evaluation of the possible adverse effects of legacy persistent organic pollutants (POPs) on the brown booby (*Sula leucogaster*) along the Brazilian coast

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ABSTRACT

This study aimed to investigate the impact of contamination by persistent organic pollutants (POPs) on Brazilian wildlife. The concentrations of certain POPs, including dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs), in the eggs of the brown booby (*Sula leucogaster*) were measured. The eggs were collected from breeding colonies located on three archipelagos (Saint Peter and Saint Paul, Abrolhos and Cagarras Islands) in the Atlantic Ocean, which are located at different distances from the Brazilian coast (range 4–1010 km). In addition, possible alterations in eggshell characteristics were evaluated. The average values of POPs found in eggs from the archipelago of Saint Peter and Saint Paul ($0.05 \mu\text{g g}^{-1}$ of ΣPCBs and $0.01 \mu\text{g g}^{-1}$ of ΣDDT) and the archipelago of Abrolhos ($0.19 \mu\text{g g}^{-1}$ of ΣPCBs and $0.03 \mu\text{g g}^{-1}$ of ΣDDT) were low compared to the reference values reported in the literature. In contrast, the concentrations measured in eggs from Cagarras ($8.4 \mu\text{g g}^{-1}$ of ΣPCBs and $1.8 \mu\text{g g}^{-1}$ of ΣDDT) were the highest, and this total PCB level is close to the threshold values considered to be harmful to birds. Our findings indicate that the brown booby colony closest to the Rio de Janeiro coast has recently been exposed to DDT. Despite the high pollution levels found on the Cagarras Islands, no alterations in the eggshell weight or the thickness of the analyzed eggs were detected. Hence, more detailed studies are recommended to determine the actual effects of the selected POPs on the Cagarras breeding colony.

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1. Introduction

In 1967, Ratcliffe reported the first case of eggshell thinning in *Accipiter nisus*, *Falco peregrinus* and *Aquila chrysaetos* and suggested that this thinning was caused by chemical substances such as dichlorodiphenyldichloroethylene (DDE), known to be one of the main metabolites of dichlorodiphenyltrichloroethane (DDT) (Ratcliffe, 1967). Since then, numerous authors have reported reduced reproductive success in many bird species as a result of eggshell thinning, altered breeding behavior and teratological malformations caused by DDE and polychlorinated biphenyls (PCBs) (Cooke, 1973, 1979a,b; Jefferies and French, 1971; McArthur et al., 1983; Fry, 1995; Peakall and Lincer, 1996). These substances are known to be persistent toxic substances (PTSs) and are included in the list of Stockholm Convention persistent organic pollutants (POPs) (http://www.chem.unep.ch/pts/gr/Global_Report.pdf).

Despite the high diversity of avifauna in Brazil, little is known about the contamination of these substances and their potential

negative effects on bird populations. To date, a single report concerning POP contamination in the muscles of brown boobies (*Sula leucogaster*) collected from the archipelago of Saint Peter and Saint Paul remains the only available source of information (Weber, 1983).

Marine birds are well known as appropriate organisms for bio-monitoring purposes because of the high trophic position of these birds in the food chain, which leads to the accumulation of POPs that are present in the environment. In turn, POPs can be transferred from the birds to their eggs and offspring, which can provide a means for observing the effects of these pollutants on the reproductive processes of bird colonies (Vermeer and Peakall, 1977; Walker, 1990; Burger and Gochfeld, 2004).

The brown booby (*S. leucogaster*) is found in tropical and subtropical regions and is the species with the maximum number of individuals in the Sulidae family (Nelson, 1978). This species breeds in colonies along the Brazilian coast, facilitating sample collection from many different regions and the assessment of geographical factors and distributions. Brown boobies spend their initial years traveling across large ranges, up to 2000 km away from their hatching site, but brown boobies tend to return to their natal colonies to breed after approximately 3 years (Nelson, 1978; Baumgarten, 2003). During the breeding season, brown boobies forage primarily

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on flying fish and squid located in the vicinity of the breeding colony (Kohlrausch, 2003; Alves et al., 2004; Coelho et al., 2004). As a top predator, the brown booby possesses a high potential for the biomagnification of POPs (Nelson, 1978).

Females normally lay two eggs, but only one chick is raised because the first chick to hatch removes the other egg from the nest. This second egg is considered as security in case of the loss of an egg, enabling the uninterrupted continuity of the breeding process (Simmons, 1967).

Due to their tendency to biomagnify and their high persistence in the environment, DDTs and PCBs (both POPs) have been extensively studied (D'Amato et al., 2002; Torres et al., 2002; Almeida et al., 2007; Azevedo-Silva et al., 2007). POPs are also semi-volatile, which facilitates their movement across long distances in the atmosphere before their deposition (Wania and Mackay, 1993).

In Brazil, restrictions on the use of DDT in agriculture were first implemented in 1971, and the regulations gradually became stricter until a total ban was declared in 2009 (http://www.planalto.gov.br/ccivil_03/_Ato2007-2010/2009/Lei/L1936.htm; D'Amato et al., 2002). The production, commercialization and use of PCBs in Brazil were prohibited in 1981; however, the use of dielectric fluids containing PCBs is permitted in older equipment until these PCBs are replaced by other substances (Azevedo-Silva, 2004).

The objective of this study was to investigate the contamination by POPs along the Brazilian coast and the possible effects of POPs on Brazilian wildlife. Therefore, we determined the concentrations of selected POPs, including DDT and PCBs, in the eggs of brown boobies from three different breeding colonies located along the Brazilian coast. The potential environmental effects of these POPs on brown booby reproductive parameters were also considered.

2. Materials and methods

2.1. Study area

Samples of brown booby eggs were collected from three archipelagos located along the Brazilian coast (Fig. 1).

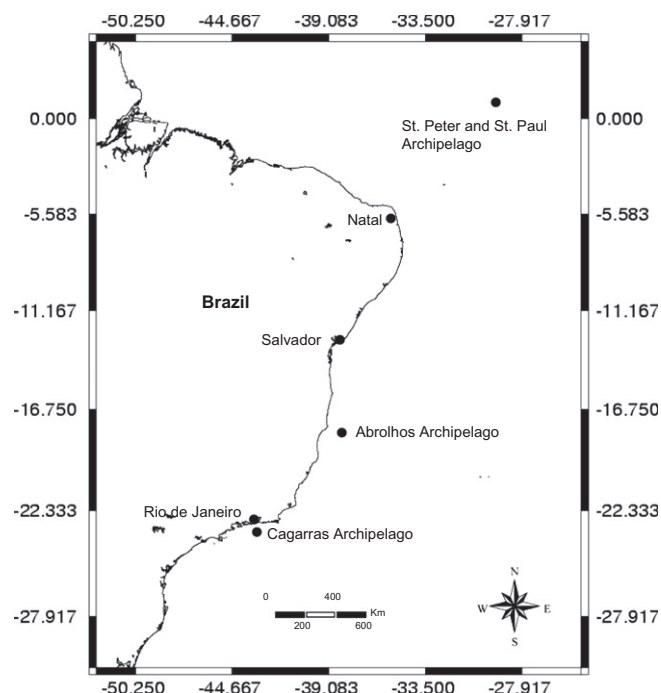


Fig. 1. Locations of the three study sites of brown booby (*Sula leucogaster*) breeding colonies and the largest urban center closest to each colony.

The Saint Peter and Saint Paul archipelago (00°55'N and 29°21'W) is composed of five rocky islets in the Atlantic Ocean that are located 1010 km from the city of Natal in the northeastern region of Brazil (Moraes, 1996). The islands are the summit of a submerged mountain, the base of which is 4000 m below the sea level (Kohlrausch, 2003). There are no sandy beaches or sources of drinking water and there is very little grassy vegetation at the summit of the main island (Both, 2001). The archipelago was declared an environmentally protected area in 1986, and a scientific research station was constructed in 1998; only authorized individuals are permitted on these islands (Souza, 2007).

The archipelago of Abrolhos (17°58'S and 38°42'W) is located 70 km from the southern portion of the Bahia State and consists of five volcanic islets. All but the smallest islet have sandy beaches; there are no sources of drinking water and the vegetation is composed of grasses, shrubs and exotic vegetation (Ibama-Funatura, 1991). This archipelago is one of the main breeding sites for marine birds along the Brazilian coast (Baumgarten, 2003). In 1983, this archipelago was declared a national marine park (http://www.ibama.gov.br/parna_abrolhos). Despite various conservation efforts, the population of goats, most likely introduced to the main island by sailors in past centuries (Ibama-Funatura, 1991), is likely to have an impact on the breeding colony of brown boobies on that island.

The archipelago of Cagarras consists of four islands and two islets (23°02'S and 43°12'W), which are located 4 km off the coast of the city of Rio de Janeiro. There are no sandy beaches and there is no source of drinking water; the vegetation is composed of herbs and shrubs with some trees (Rodrigues et al., 2007). In April 2010, this archipelago was declared a natural monument, with the intention of protecting the archipelago against any activities that may put the fauna and flora at risk (http://www.planalto.gov.br/ccivil_03/_Ato2007-2010/2010/Lei/L12229.htm). Despite considerable efforts to protect this important breeding site, the islands are greatly impacted by their proximity to the large urban center of the city of Rio de Janeiro; regular visits by anglers and tourists, who leave a large amount of garbage behind, cause a disturbance to the breeding birds (Rodrigues et al., 2007). Furthermore, the archipelago is impacted by the discharge of $6.5 \text{ m}^3 \text{ s}^{-1}$ of domestic sewage at a location just 2 km away from the islands (Rangel et al., 2007), as well as the proximity of the island to the entrance of Guanabara Bay (9 km). Five hundred tons of untreated domestic and industrial sewage and 6.9 tons of oil are discharged daily into the bay from 12 counties that altogether correspond to a population of 14 million inhabitants (Lailson-Brito et al., 2010).

2.2. Egg sampling

Egg samples were collected between January and May 2007. A total of eight eggs were collected from each archipelago. To ensure that the reproductive potential of each nest was maintained, only one egg was collected per nest. Only freshly laid eggs were collected, and the immersion technique was used to determine whether the collected eggs were fresh (Castiglioni and Gonzaga, 1999). Immediately after collection, the eggs were wrapped in aluminum foil and kept refrigerated in the field. The eggs were stored at -20°C until residue analysis. Due to the high lipid content of the eggs, only the yolks were analyzed.

2.3. Materials

The following standards: *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, polychlorinated biphenyls (PCBs) # 28, 52, 95, 101, 105, 114, 118, 123, 132, 138, 149, 153, 156, 157, 167, 170, 180, 183, 189, 194 and 209 and 1,2,3,4-tetrachloronaphthalene (TCN) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All of the solvents used were of pesticide residue analysis or equivalent quality, including

the dichloromethane and n-hexane from Tedia Inc. (Fairfield, Ohio, US).

2.4. Analytical procedures

Approximately 3 g of yolk was extracted in a Soxhlet apparatus for 8 h with dichloromethane and n-hexane (1:1). Sulfuric acid digestion was used to remove the fat present in the samples. Fractionation was performed using an open glass chromatographic column filled with 4 g of Florisil and topped with 2 g of anhydrous sodium sulfate. The first fraction was eluted with 11.5 mL of n-hexane, and the second fraction was eluted with 15 mL of n-hexane:dichloromethane (1:1).

2.5. Instrumental analysis

Concentrations of DDTs and PCBs were determined by HRGC-ECD on a Hewlett Packard 6890 GC equipped with a ^{63}Ni μ -electron capture detector. A BPX5 capillary column (60 m \times 0.25 mm i.d.; 0.25 μm film thickness), purchased from SGE (Melbourne, Australia), was used. The carrier gas was nitrogen at a head pressure of 192.2 Kpa. The detector and injector temperatures were 300 °C and 270 °C, respectively. For quantification purposes, a seven-point calibration curve was constructed for each target analyte using TCN and PCB 209 as internal standards. The average limits of detection (LOD), calculated as three times the signal-to-noise ratio, ranged from 0.01 ng g⁻¹ (PCB 118) to 0.30 ng g⁻¹ (PCB 194) for PCBs and the LODs ranged from 0.08 ng g⁻¹ (*p,p'*-DDE) to 0.37 ng g⁻¹ (*p,p'*-DDT) for DDT. Further details on the determination and quantification of PCBs and DDT can be found in Roscales et al. (2010). Quality control and assurance measures included the analysis of blank samples (one procedural blank in each set of six samples) and daily checks of the calibration curves. The PCB and DDT concentrations are expressed as their wet weight (w/w), unless otherwise stated.

2.6. Eggshell preparation and analysis

After removing the contents of the eggs, the eggshells were washed in tap water and then dried at room temperature. Measurements of the eggshell thickness were obtained using a digital caliper Mitutoyo (SP, Brazil) with a 0.02 mm accuracy. The mean values of four measurements taken from the equatorial region of the shells were used for statistical analyses. The measurements of the length, width and weight of the eggs obtained at the time of collection and the weights of the dried shells were used for the calculation of Ratcliffe's index (Ratcliffe, 1967).

3. Results

All of the eggs sampled from the three locations in this study demonstrated PCB contamination. Up to 12 different PCB congeners were measured in the eggs from the Saint Peter and Saint Paul archipelago, while all 18 congeners analyzed in this study were detected in the eggs from both the Abrolhos and Cagarras archipelagos. DDT and its metabolites were found in all of the egg samples. The ranges, mean concentrations and median values are shown in Table 1.

The eggs collected at the Saint Peter and Saint Paul archipelago had the lowest ΣPCBs (the sum of all of the PCB congeners analyzed) and ΣDDTs (the sum of DDT and its metabolites) concentrations. The PCB and DDT concentrations in the eggs from the Abrolhos archipelago were slightly higher than those recorded in the eggs from the Saint Peter and Saint Paul archipelago. The eggs from the Cagarras archipelago had the highest PCB and DDT concentrations.

At all of the locations, the eggs with the highest ΣPCBs concentrations also had the highest ΣDDTs contamination.

A normal distribution for the pollutant concentrations (Shapiro–Wilk, all $p < 0.05$) was not recorded for any of the three sampled locations. However, a significant difference was found for the pollutant concentrations among the locations sampled (Kruskal–Wallis, $p \leq 0.001$). The Duncan test indicated that the mean concentrations of both the ΣDDTs and the ΣPCBs in the eggs from the Cagarras archipelago were significantly different from those in the eggs from the other two locations ($p < 0.05$).

The values of eggshell weight, eggshell thickness and Ratcliffe's index were normally distributed (Table 1). The highest values for all of these measurements were found for the eggs from the Saint Peter and Saint Paul archipelago. The eggs from the Cagarras and Abrolhos archipelagos had lower values (Table 1). A significant difference was found for these eggshell measurements among the three different locations (ANOVA, $p \leq 0.001$). All of the measurements of the eggs from the Saint Peter and Saint Paul archipelago were significantly different from the measurements of the eggs from Abrolhos and Cagarras (Tukey Test, $p < 0.001$). However, there were no significant differences between the measurements of the eggs from Abrolhos and Cagarras.

No significant correlations were found between the concentration of DDE and variables such as egg weight, shell thickness, or Ratcliffe's index (Spearman Test, $p > 0.05$). However, all of the correlation coefficients with the ΣPCBs were negative (weight: $r_s = -0.547$, thickness: $r_s = -0.591$ and Ratcliffe's index: $r_s = -0.569$), with p values lower than 0.05 (p (weight) = 0.006, p (thickness) = 0.002 and p (Ratcliffe's index) = 0.004).

4. Discussion

The DDT and PCB concentrations measured in the present study only reflect the contamination of females at each sample site and at one specific period. Differences in gender, foraging habits and fish availability throughout the year as well as external influences of foraging behaviors (fisheries activities) may represent bias in the study results. However this is the first study to report and compare the contamination by POPs at three different sites along the Brazilian coast.

To date, there is limited information available concerning the presence and impact of POPs in the eggs of marine birds of the Sulidae family in the southern hemisphere, and data regarding the presence and impacts of these pollutants on the bird populations of Brazil are even more scarce. In fact, the analysis of one egg sample of *S. leucogaster* by Weber (1983), which was collected from the Saint Peter and Saint Paul archipelago in 1979 (0.09 $\mu\text{g g}^{-1}$ of ΣPCBs and 0.04 $\mu\text{g g}^{-1}$ of ΣDDTs), is the only information available to date. The concentrations that Weber measured are higher than the mean concentrations found in the present study (0.05 $\mu\text{g g}^{-1}$ of ΣPCBs and 0.01 $\mu\text{g g}^{-1}$ of ΣDDTs). However, comparisons should be made with caution because of the differences in the analytical methods and the small sample size of the former study.

In the study conducted by Elliott et al. (1988) on the northern gannet (*Morus bassanus*), it was not possible to separate the effect of high PCB concentrations (23.9 $\mu\text{g g}^{-1}$) from the effects of other pollutants examined. However, according to Elliott et al. (1988), the possible negative effect of PCBs on the hatching rate of the northern gannet could not be disregarded. In studies conducted between 1986 and 1988 in the North American Great Lakes, the eggs of the reproductive colonies of *Phalacrocorax auritus* were found to have high concentrations of PCBs. It was suggested that PCB concentrations of 14.8 $\mu\text{g g}^{-1}$ and greater were responsible for the toxic effects observed, such as high embryonic and juvenile death rates and genetic malformations (Tillitt et al., 1992).

Table 1
The Σ PCBs, Σ DDTs and DDE concentrations (in $\mu\text{g g}^{-1}$ on wet weight basis), and the eggshell thicknesses, weights and Ratcliffe's indices measured for the eggs from each study location ($n = 8$ per sampling location).

Sampling location		Σ PCBs	Σ DDTs	DDE	Thickness (mm)	Weight (mg)	Ratcliffe index
St. Peter and St. Paul	Range	0.02–0.10	0.01–0.03	0.01–0.03	0.51–0.57	7011.80–7958.00	2.44–2.84
	Mean	0.05	0.01	0.01	0.54	7489.55	2.72
	Median	0.04	0.01	0.01	0.53	7522.10	2.77
Abrolhos	Range	0.10–0.40	0.01–0.10	0.01–0.05	0.39–0.46	4278.50–5822.30	1.94–2.31
	Mean	0.20	0.03	0.02	0.42	5106.39	2.06
	Median	0.10	0.02	0.02	0.43	5167.10	2.11
Cagarras	Range	5.58–12.56	1.15–2.73	0.60–1.50	0.40–0.52	4937.20–6212.60	1.98–2.48
	Mean	8.40	1.80	1.02	0.45	5558.13	2.19
	Median	8.00	1.60	0.90	0.44	5623.65	2.21

The PCB levels found in the eggs collected from Cagarras for this study are similar and within the same order of magnitude as those reported to be a concern for *M. bassanus* and *P. auritus*. Considering that this study is focused on a different species (the brown booby), more detailed studies on the reproductive success of this species are necessary to identify whether the observed PCB levels have a negative influence on the reproductive success of the brown booby.

Information concerning the amount and composition of the commercial PCBs used in Brazil is scarce (Penteado and Vaz, 2001). Most of the PCBs used in Brazil came from Aroclor 1254, which was imported from United States. In Brazil, Aroclor 1254 was commercialized with the name of Ascarel, a mixture composed 75% of Aroclor 1254 and 25% trichlorobenzene (Antonello et al., 2007). Other mixtures known as Ascarel type A (composed of 60% of Aroclor 1260 and 40% trichlorobenzene) and Ascarel type B (composed of 70% of Aroclor 1254 and 30% trichlorobenzene) were also available (Antonello et al., 2007).

Considering the composition of the Σ PCBs at each study site, the PCB congeners containing five, six and seven chlorine atoms predominate, representing more than 90% of the mean PCB concentration measured (Fig. 2), suggesting that Aroclor 1260 was the main mixture encountered in the analyzed samples. These congeners are less volatile and have low atmospheric dispersion rates (Wania and MacKay, 1993). The contamination of remote areas, such as the Saint Peter and Saint Paul and Abrolhos archipelagos, may be explained by the fact that these congeners are resistant to metabolic or environmental degradation, facilitating their transport across long distances via atmospheric, marine, or biological means. Low-chlorinated congeners were found at low concentrations in the eggs from only two locations, and the concentration of these congeners

increased with increasing proximity to the mainland (2.4% and 6.3% of the Σ PCBs in the eggs from the Abrolhos and Cagarras Islands, respectively).

Seven PCB markers (# 28, 52, 101, 118, 138, 153 and 189) comprised more than 60% of the average PCB concentration measured in the eggs from each location (83% at St. Peter and St. Paul, 61% at Abrolhos and 69% at Cagarras). PCB markers # 101, 118, 138, 153 and 189 were found in eggs from all of the locations; PCB 153 was the most abundant when considering only these seven marker PCBs (Fig. 3).

Of the twelve existing dioxin-like PCBs, eight were analyzed in this study (# 105, 114, 118, 123, 156, 157, 167, 189). PCB 157 was not found in eggs from any of the studied locations. In contrast, PCB 167 was the marker found in the highest concentration in eggs from both the St. Peter and St. Paul and Abrolhos archipelagos. Considering all of the PCBs analyzed in this study, PCB 167 was the congener with the highest concentration found in the eggs from Abrolhos.

4.1. DDT/PCB ratios

The ratio between DDT and PCB concentrations has been used to characterize the degree to which agricultural sources contribute these pollutants in comparison to industrial sources. At the three study locations, industrial sources of pollution were more important, as indicated by the higher content of Σ PCBs compared to Σ DDTs (Fig. 4). This observation was reflected in the Σ DDT/ Σ PCB ratios, which were 0.38, 0.15 and 0.22 for the eggs from the Saint Peter and Saint Paul, Abrolhos and Cagarras archipelagos, respectively.

Similar trends were found in other studies conducted near the study area considered in this study. For example, sediment samples from a mangrove swamp located close to a very industrialized area inside of Guanabara Bay had Σ DDTs of $0.04 \mu\text{g g}^{-1}$ dry weight

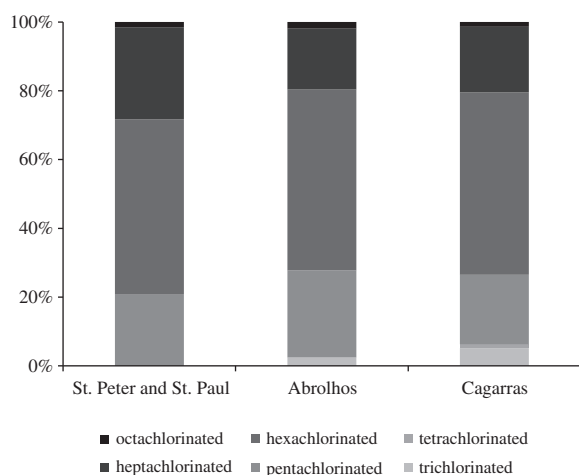


Fig. 2. Percentage that each PCB congener group contributed to the Σ PCBs in the eggs from each study site.

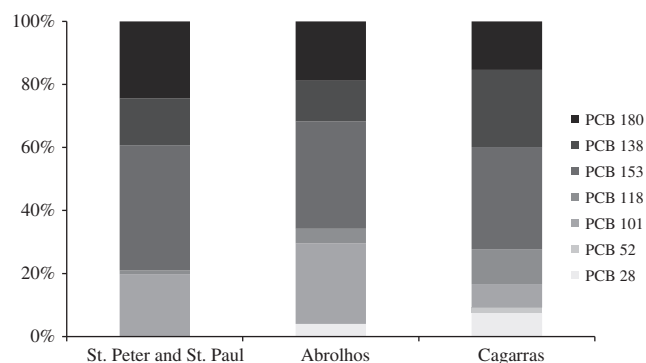


Fig. 3. Percentages of each of the seven PCB markers (28, 52, 101, 118, 138, 153 and 189) in the eggs from each study site, when considering only this group of PCBs.

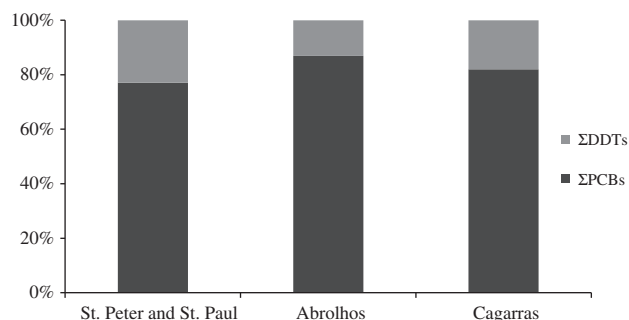


Fig. 4. Ratio between the mean concentrations of the ΣDDTs and the ΣPCBs in the brown booby (*Sula leucogaster*) eggs from each study sites.

(d.w.) and ΣPCBs of $0.2 \mu\text{g g}^{-1}$ d.w. (Souza et al., 2008). Souza et al. (2008) also observed that the eggs of crabs (*Chasmagnathus granulata*) inhabiting the same mangrove swamp contained ΣDDTs of $0.1 \mu\text{g g}^{-1}$ d.w. and ΣPCBs of $0.6 \mu\text{g g}^{-1}$ d.w. Furthermore, the blubber of Guiana dolphins (*Sotalia guianensis*) from Guanabara Bay had $8 \mu\text{g}$ of ΣDDTs per g lipid weight (l.w.) and $34.8 \mu\text{g}$ ΣPCBs per g l.w. (Lailson-Brito et al., 2010). The ratios of ΣDDTs/ΣPCBs in the samples from these three species were 0.20, 0.17 and 0.23, respectively, which are very similar to the ratio found for the eggs from the Cagarras archipelago, which is located 2 km from the entrance to Guanabara Bay.

4.2. Ratio of *p,p'*-DDE/ΣDDT

Technically, DDT is predominantly composed of *p,p'*-DDT. When this substance is released into the environment, it degrades into *p,p'*-DDE and *p,p'*-DDD. Traditionally, the ratio of *p,p'*-DDE/ΣDDT has been used to discriminate between recent and past usages of DDT. Low *p,p'*-DDE/ΣDDT ratios indicate the recent use of DDT.

The data obtained in the present study show that, the ratio of *p,p'*-DDE/ΣDDT in brown booby eggs was 0.8 at the Saint Peter and Saint Paul and Abrolhos archipelagos and 0.5 at Cagarras. This information suggests that the brown booby colony located close to the Rio de Janeiro coast (i.e., Cagarras) has been more recently exposed to this pesticide in comparison with the other two colonies (Fig. 5).

4.3. Variations in eggshell parameters and contaminant levels

While studying the effect of DDE on different species of sea-birds, Cooke (1979a) observed that the main effect of this DDT metabolite on the structure of northern gannet eggshells was a decrease in the thickness of the outer shell. Elliott et al. (1988) observed a decrease in this layer in eggs from the same species that contained $4.35 \mu\text{g g}^{-1}$ DDE. However, a population decline due to eggshell thinning through the loss of the protective outer layer

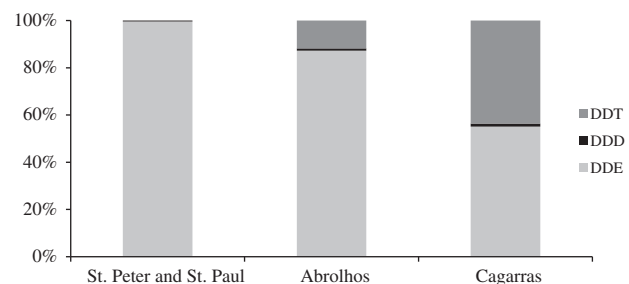


Fig. 5. Contributions of DDE, DDD and DDT to the ΣDDTs content in the brown booby (*Sula leucogaster*) eggs from each study sites.

has only been recorded to occur when the DDE concentration exceeds $18.5 \mu\text{g g}^{-1}$. When DDE concentrations higher than this level were measured, the eggshell thickness was reduced by 17%, and the hatching success was only 38% (Elliott et al., 1988). In 1979, Morrison calculated the Ratcliffe's indices for *S. leucogaster* and *Sula dactylatra* eggs collected along the Pacific coast prior to 1947 and after 1948 (when the use of DDT was extended). Both species exhibited significant reductions in eggshell thickness, with that of brown booby eggs decreasing by 7.9%. A more recent study that analyzed brown booby eggs collected from colonies along the Mexican coast in 2006 reported very low concentrations of DDE, with a southeast–northwest trend of an increase in concentration (0.01 – $0.05 \mu\text{g g}^{-1}$ of DDE), which corresponded to the use of DDT in the 1970s (Mellink et al., 2009). According to the authors, these values represented a healthy near-shore marine environment in relation to the level of organochlorine contamination. This finding is reinforced by the recovery of eggshell thickness to pre-DDT levels at a colony where the analyzed eggs could be compared to the museum collections of eggs collected from the same site.

The DDE concentrations found in the eggs from Saint Peter and Saint Paul and Abrolhos were very low compared to the values reported to be a concern to marine birds and most likely do not represent a risk to the reproductive success of these brown booby populations. Even the higher DDE concentration ($1.50 \mu\text{g g}^{-1}$) observed at Cagarras does not reach the levels reported to represent a risk to different bird species. Nevertheless, Blus et al. (1997) established a concentration–effect relationship between DDE concentrations and eggshell thinning that indicates that the percentage of change is greater per unit of DDE when the concentration of DDE is lower. This fact highlights the need to continue to monitor the DDT concentrations in the Cagarras colony.

The values observed for the eggshell weight and thickness and the Ratcliffe's index did not show any relationship to DDE concentrations. However, when these values were compared with PCB concentrations, negative correlations were found, suggesting that increased PCB concentrations may lead to a decrease in egg weight and eggshell thickness.

The eggs collected from the Saint Peter and Saint Paul archipelago were much larger, with heavier and thicker eggshells than the eggs collected from Cagarras, where the DDT and PCB concentrations were the highest. However, the eggs from Abrolhos, which had low DDE and PCB concentrations, were the smallest eggs with the thinnest eggshells of all three locations examined.

The significant difference between the eggs from the Saint Peter and Saint Paul archipelago and those of the Cagarras and the Abrolhos archipelagos could be explained by the geographical isolation of the Saint Peter and Saint Paul colony and the characteristic philopatry of the species (Nelson, 1978), which cause the renewal of the genetic pool to be virtually negligible and, hence, the development of distinct characteristics. According to Baumgarten (2003), genetic and morphological analyses demonstrated that the Saint Peter and Saint Paul population is distinct from the populations of Fernando de Noronha/Atol das Rocas and Abrolhos, suggesting that selection may be acting mainly on the size of the individuals. However, Baumgarten (2003) did not investigate the populations located near the coast of Rio de Janeiro. Therefore, it would be very interesting to analyze the relationship between the Cagarras and Abrolhos populations, which could explain the similarity between the egg characteristics of these two locations.

5. Conclusions

The levels of DDE found at all three sampled locations are significantly lower than the values considered to have negative effects on the reproductive success and/or to induce eggshell thinning in

other species of the *Sula* genus. The PCB levels at the Saint Peter and Saint Paul and Abrolhos archipelagos are also lower than the values observed to cause embryonic and juvenile mortality and do not seem to represent a risk to the breeding colonies assessed in the current study. However, the PCB concentrations in the eggs from the Cagarras archipelago are higher than those recorded at the other two colonies and are very close to values reported to be harmful to other fish-eating birds. More detailed studies are recommended to determine the effects of these industrial pollutants on the Cagarras breeding colony. The DDE/ Σ DDT ratio found in the eggs from Cagarras suggests the recent use of DDT. Hence, the monitoring of the levels of DDT in this colony may help to confirm the illegal use of this pesticide.

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